Methods for Ambient Speciated Mercury Monitoring

National Air Monitoring Conference

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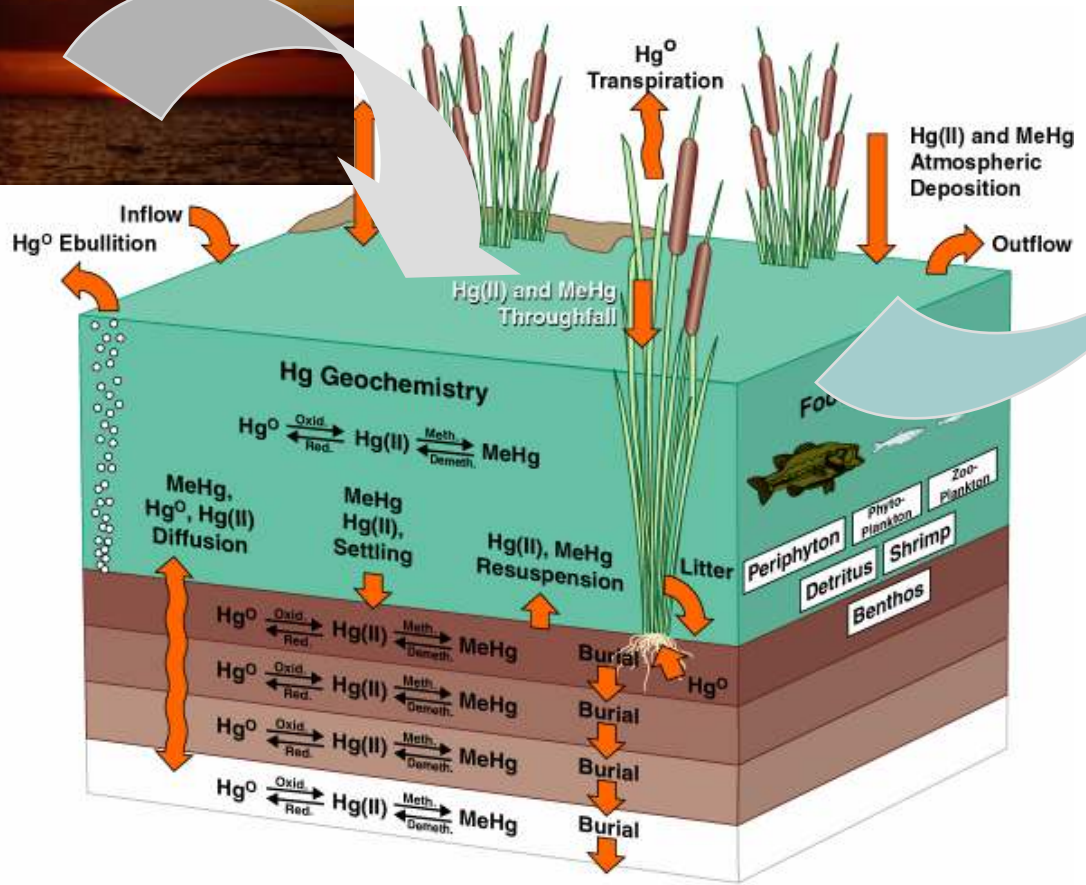
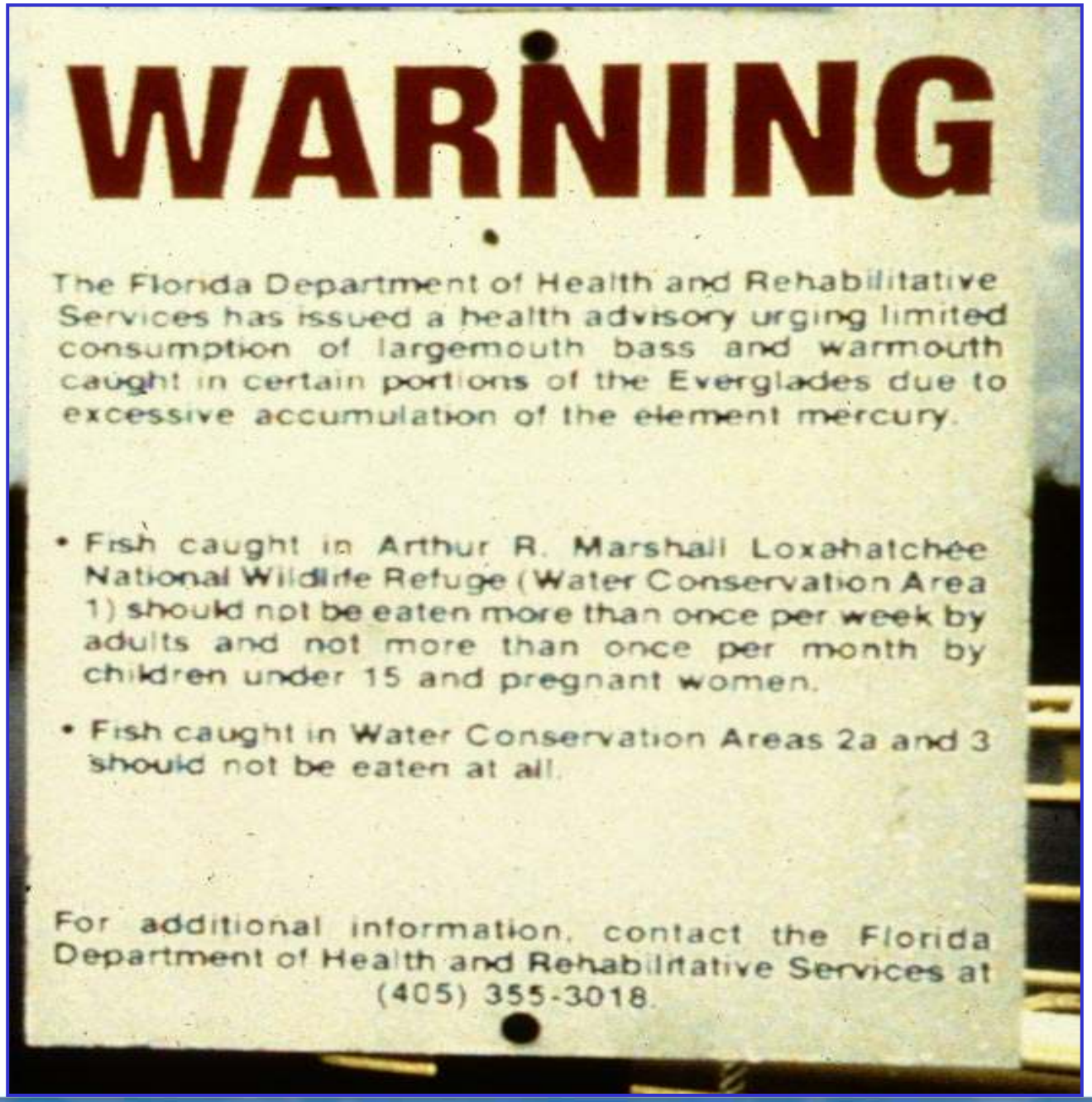

Hg^0 Transpiration
Hg(II) and MeHg Atmospheric Deposition
Inflow
Hg^0 Ebullition
Outflow
Hg(II) and MeHg Throughfall
Hg Geochemistry
Hg^0 Oxid. Red. Hg(II) Meth. Demeth. MeHg
MeHg, Hg^0, Hg(II) Diffusion
MeHg Hg(II), Settling
Hg(II), MeHg Resuspension
Litter
Periphyton
Phyto-plankton
Zoo-plankton
Shrimp
Detritus
Benthos
Burial
Hg^0


WARNING
The Florida Department of Health and Rehabilitative Services has issued a health advisory urging limited consumption of largemouth bass and warmouth caught in certain portions of the Everglades due to excessive accumulation of the element mercury.
• Fish caught in Arthur R. Marshall Loxahatchee National Wildlife Refuge (Water Conservation Area 1) should not be eaten more than once per week by adults and not more than once per month by children under 15 and pregnant women.
• Fish caught in Water Conservation Areas 2a and 3 should not be eaten at all.
For additional information, contact the Florida Department of Health and Rehabilitative Services at (405) 355-3018.


ENT IN YOUR WALLET
THURSDAY, August 10, 1989
Sentinel
RECEIVED
AUG 17 1989
ENVIRONMENTAL HAZARDS
EPIDEMIOLOGY
Mercury pollutes
3 top fishing lakes
State officials: Mercury's
effect on health unclear
Sunday, September 15, 1991 $1
BROWARD METRO
High mercury levels
taint S. Florida fish
Mercury in
North Florida
fish too high
By Carrie Teegardin
High-mercury areas

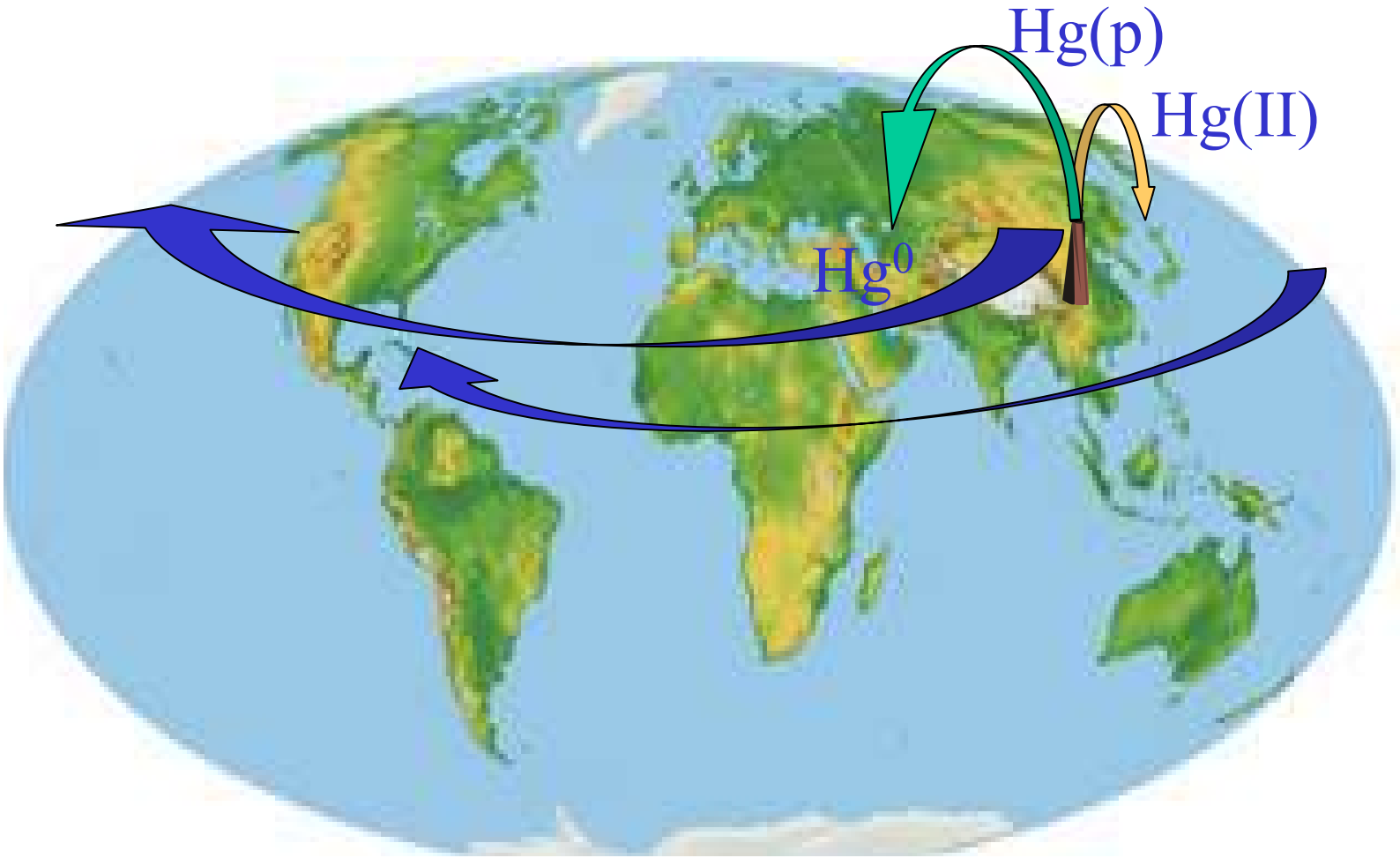
Ambient Measurements to Support Atmospheric Mercury Research

- Elucidate Atmospheric Chemistry
- Quantify Impacts from Specific Sources
- Evaluate Deterministic Models
- Provide Emission Reduction Accountability

Why Speciate Mercury?

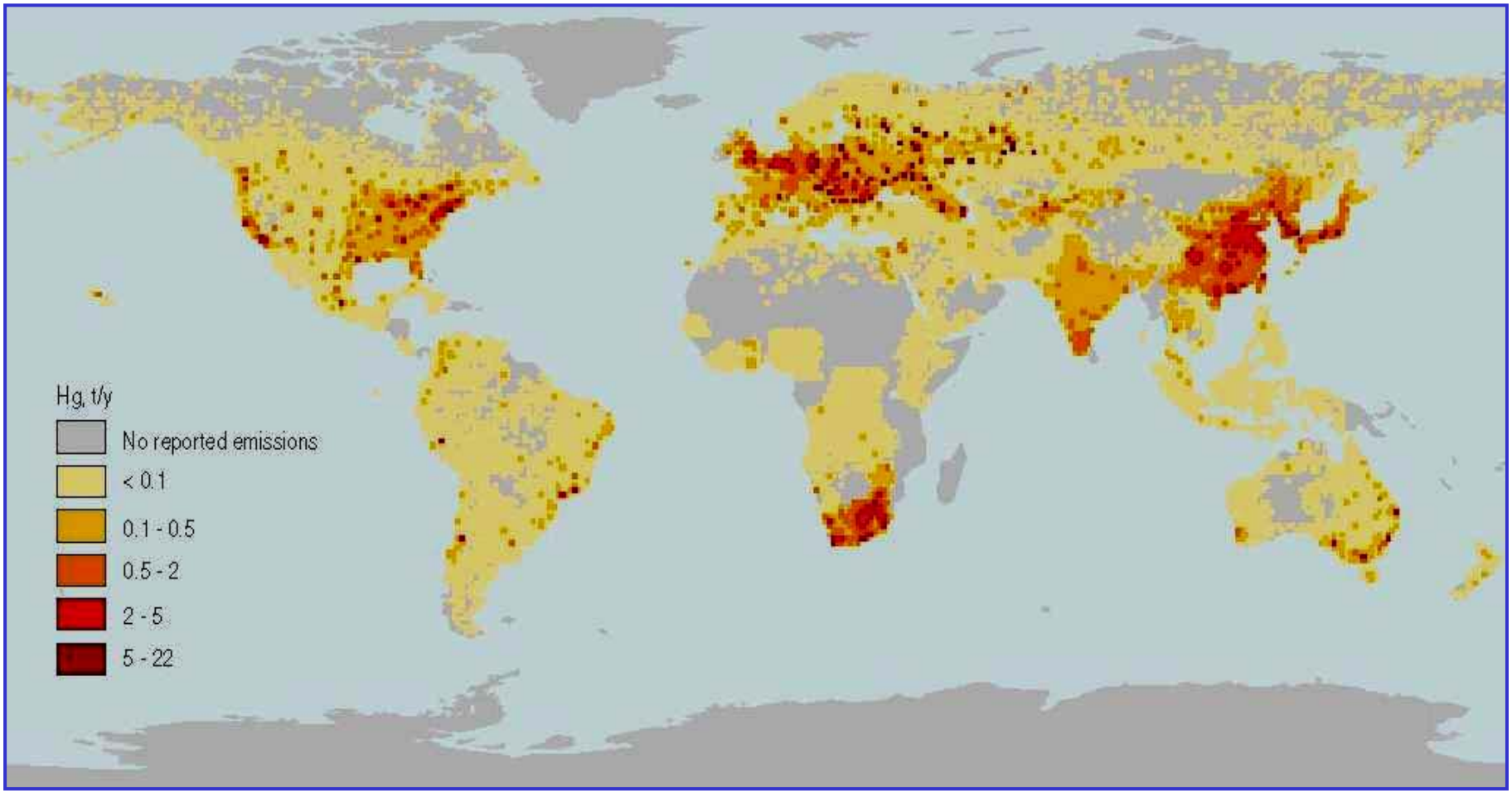
- Species have Different Behaviors
  - Elemental Mercury: Hg^0
  - Reactive Mercury: Hg^{2+}
  - Particulate Mercury: Hg(p)
- Atmospheric Transport & Deposition Modeling
- Bioaccumulation, Exposure & Risk Assessment

Contemporary Atmospheric Mercury Conceptual Model



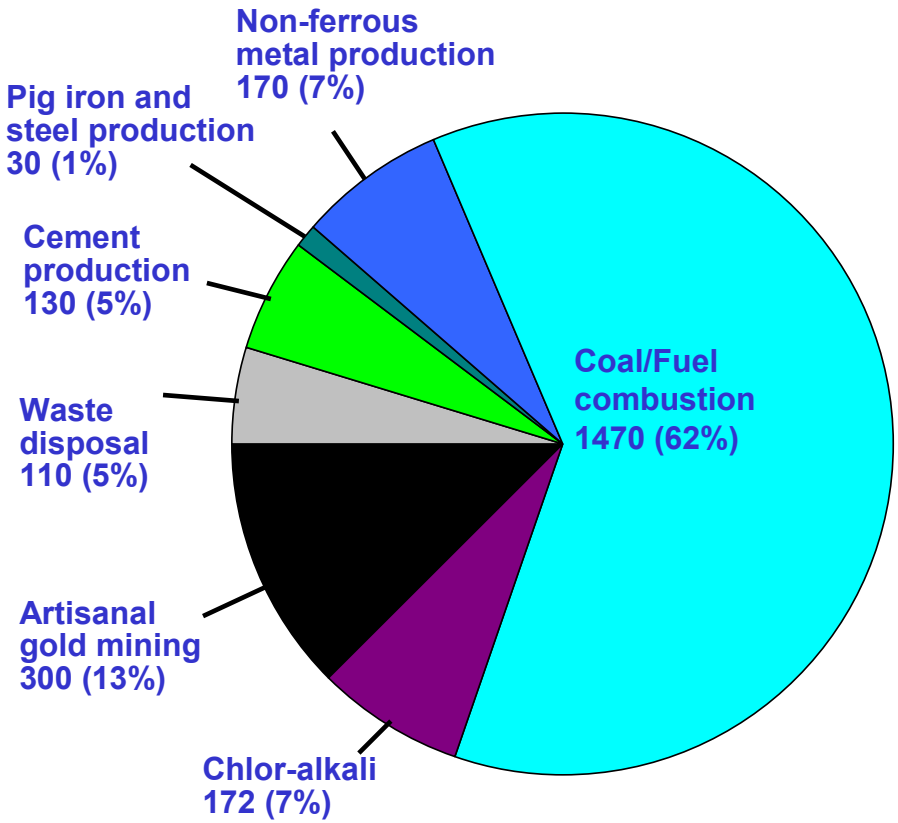
Global - Regional - Local

Spatial Distribution of Global Atmospheric Mercury Emissions



Source: UNEP Global Mercury Assessment, 2002, using J. Pacyna 1995 data, as presented by AMAP (1998)

Anthropogenic Air Emissions of Mercury: Distribution by Industrial Sector in 1995



Total: 2,382 metric tons

- **Coal and fuel combustion is by far the largest source category**
- **Estimates are rough; most countries do not have Hg inventories**
- **We need to further develop reliable emissions inventories**

Source: EPA estimates derived from UNEP Global Mercury Assessment, UNEP, Geneva, December 2002

Anthropogenic Hg Emissions Observed as Hg^{2+}

Source	N	Hg^{2+}/Total Hg(%) ± Std. Dev.
Cement Production[a]	3	25 ± 4
Incinerator (medical)[a]	3	95 ± 5
Incinerator (municipal)[a]	8	78 ± 8
Coal-fired Utility Boiler[b]	19	67 ± 27

[a] **Stevens *et al.*, 1996**

[b] **Prestbo and Bloom, 1995**

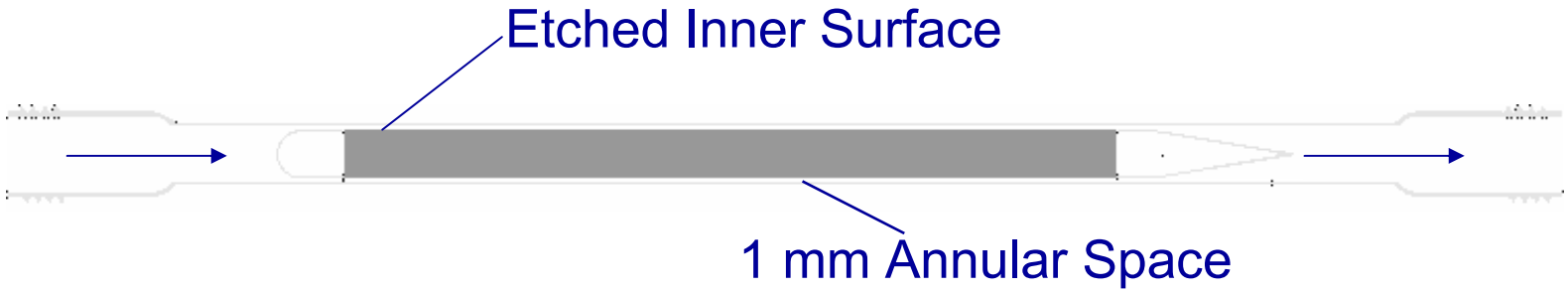
Ambient RGM Methodologies

- **Impregnated Filter**
- **Refluxing Mist Chamber**
- **Tubular Denuder**

Challenges Measuring RGM

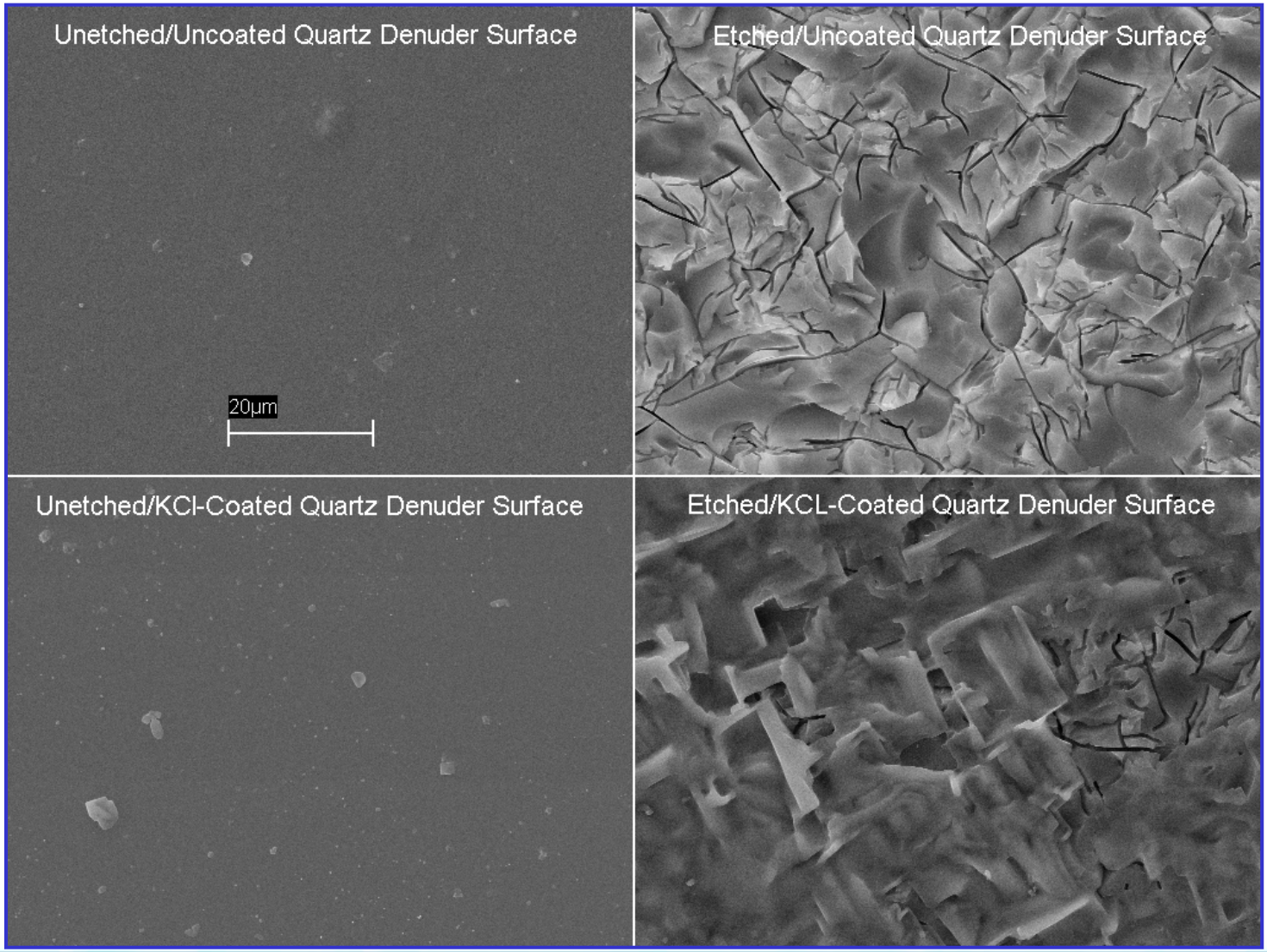
- Reject much larger *elemental* component
- Method must be 1-2 orders of magnitude more sensitive than total mercury methods
- Quantitatively pass *RGM* to the collector
- Exclude *particulate phase* mercury while avoiding filter artifact

Quartz Annular Denuder

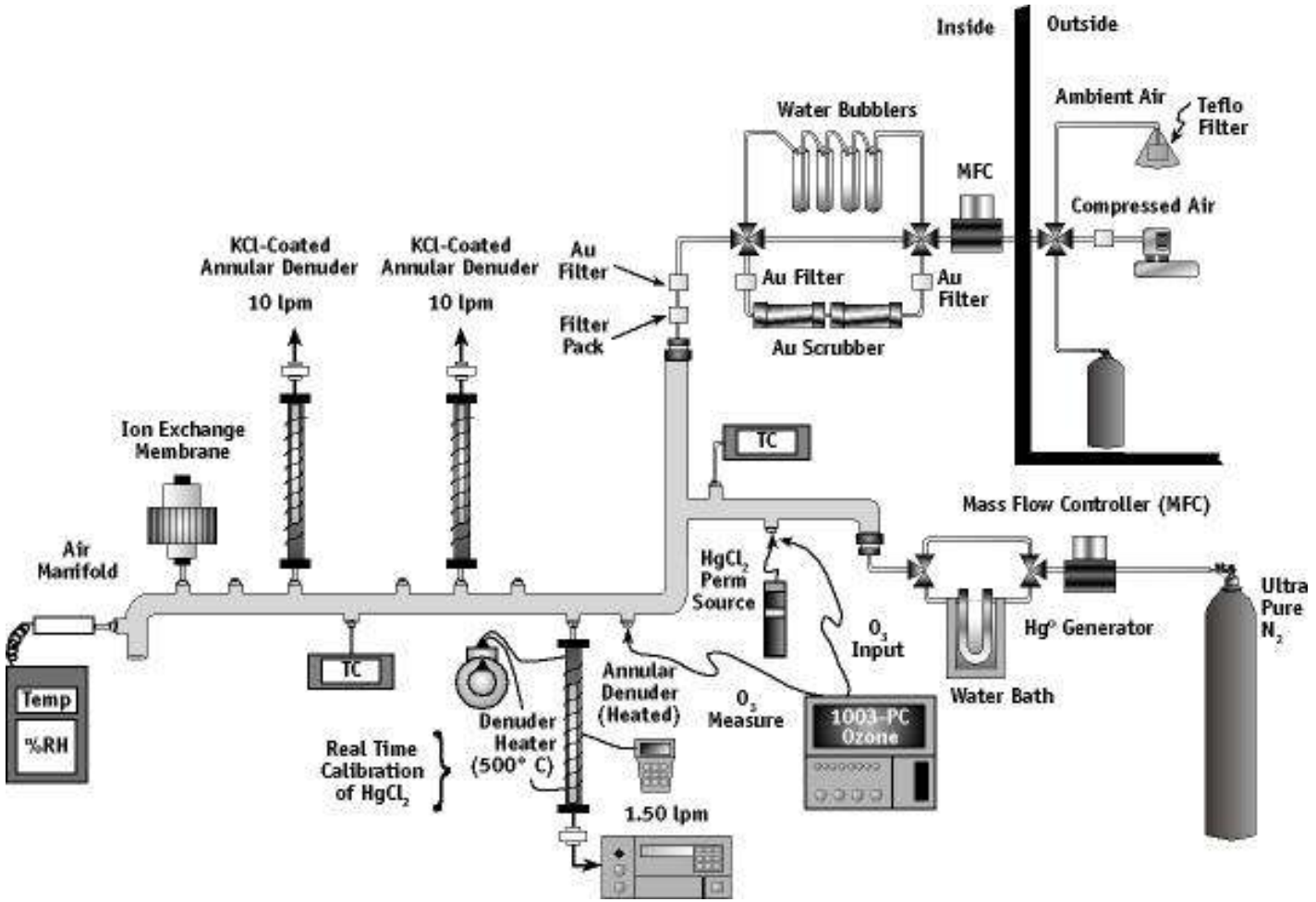


* Landis et al. *Environ. Sci. Technol.*, **2002**, 36, 3000-3009

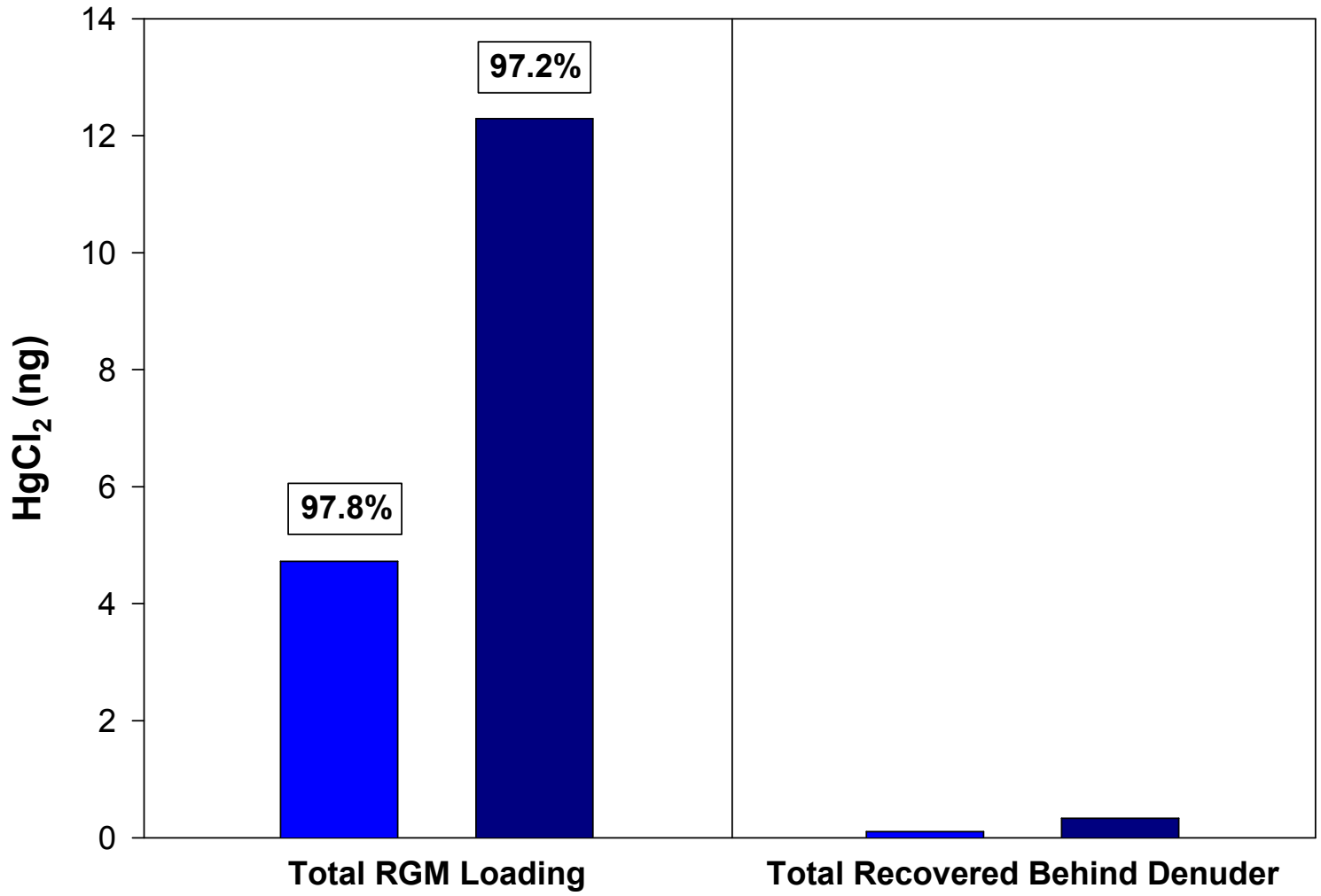
SEM Micrographs of Quartz Surfaces



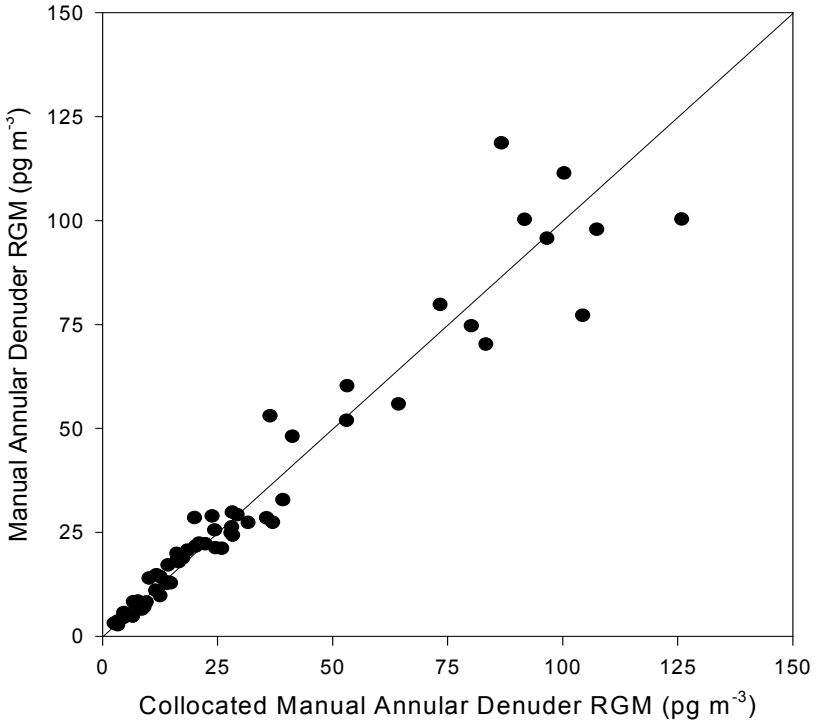
Laboratory Evaluation

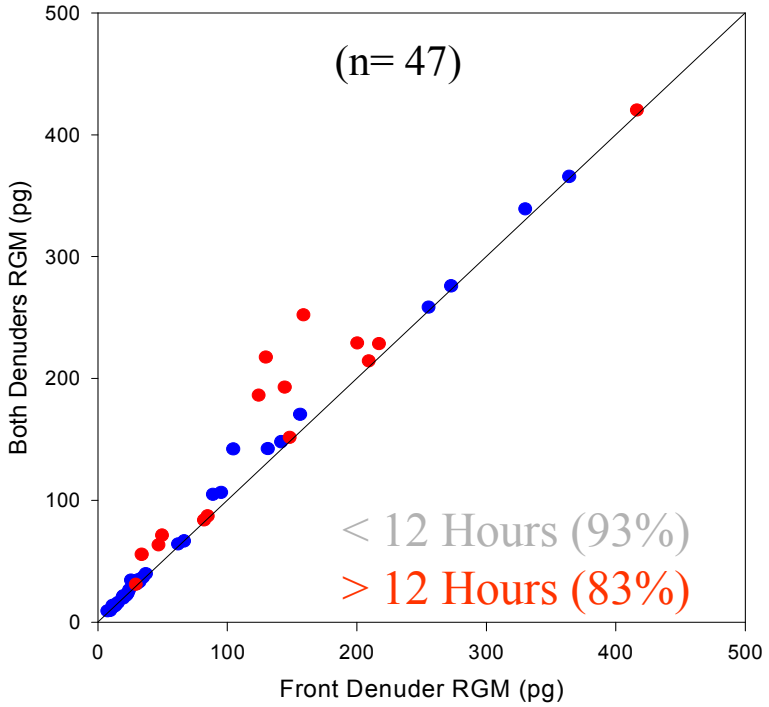


Collection Efficiency for $HgCl_2$

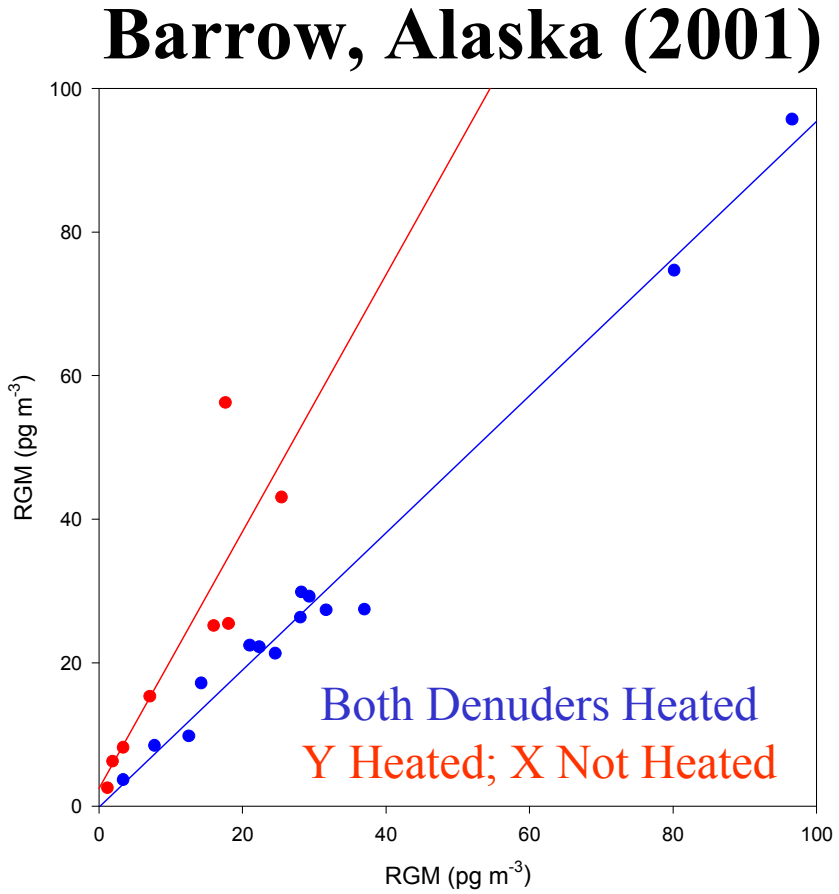


Annular Denuder Performance

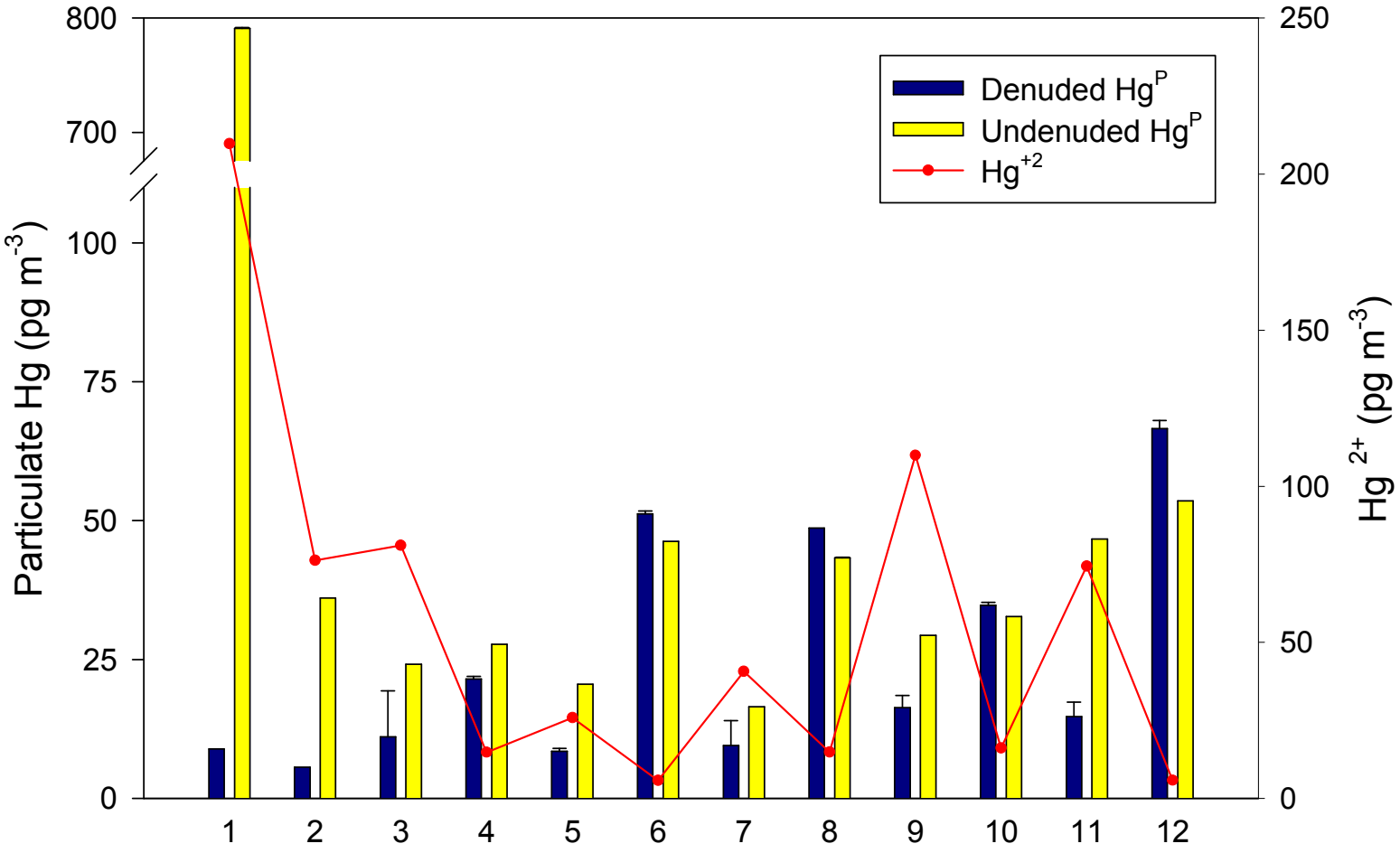




Importance of Properly Heating Sampling System



Collocated Denuded & Undenuded Hg(p)



KCl Denuder Method Detection Limits

Field Blanks

N	Mean (pg)	Std Dev (pg)
66	2.22	1.24

10 LPM Flow Rate

Duration (hours)	Air Volume (m^3)	MDL (pg m^{-3})
1	0.6	4.1
2	1.2	2.1
6	3.6	0.7
12	7.2	0.3

Observed RGM Concentrations

Site	N	Mean (pg m^{-3})	Min (pg m^{-3})	Max (pg m^{-3})	Std Dev (pg m^{-3})
Baltimore, MD	30	22.7	5.4	138.7	25.9
Everglades, FL	45	15.4	2.5	54.3	12.0
RTP, NC	26	15.5	3.5	51.0	12.0

Field Monitoring Setup

Manual Denuder Sampling Box

Quartz Thermal Filter Pack

Standard Filter Pack

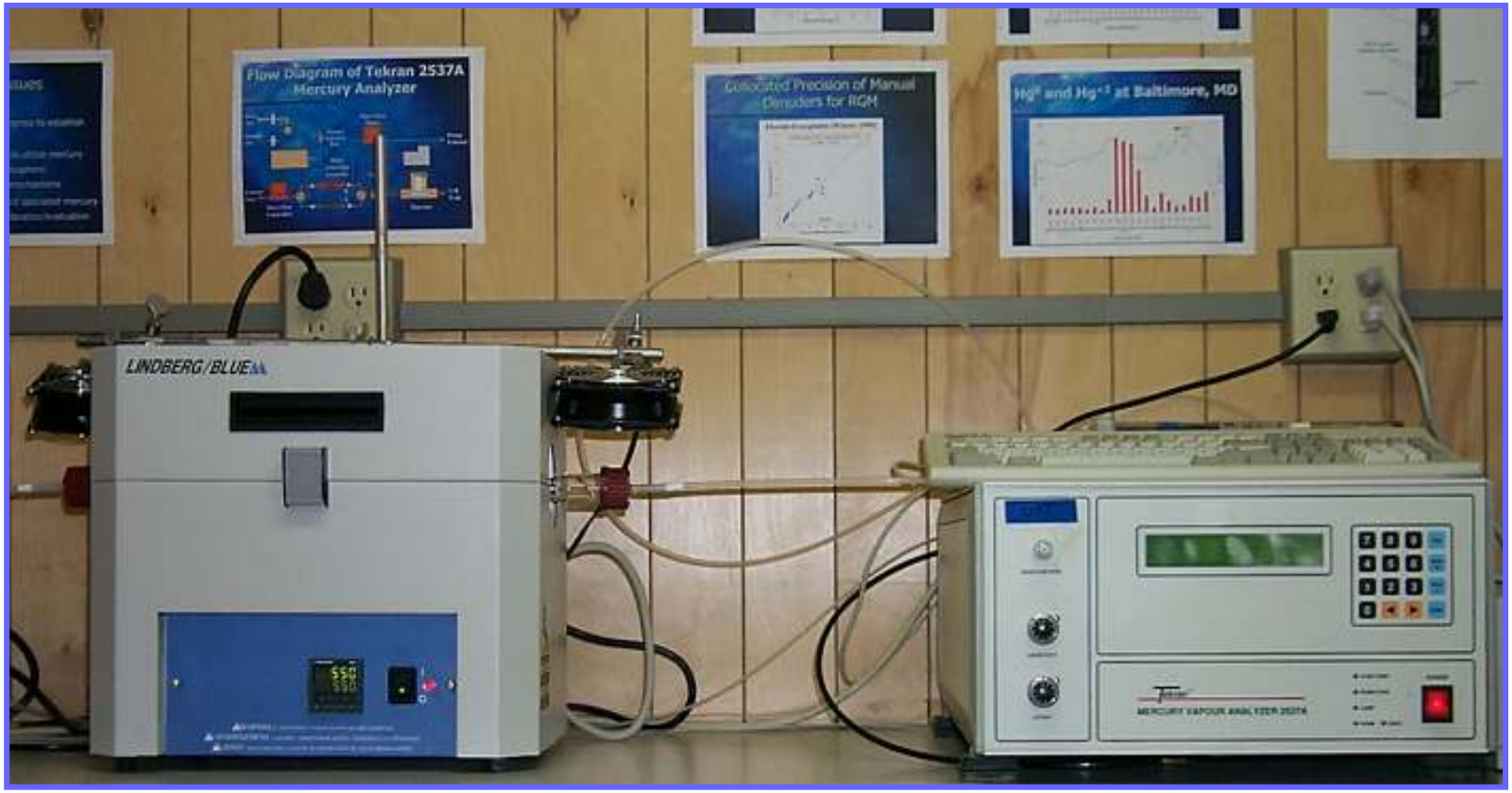
KCL - coated Annular Denuders

Elutriators

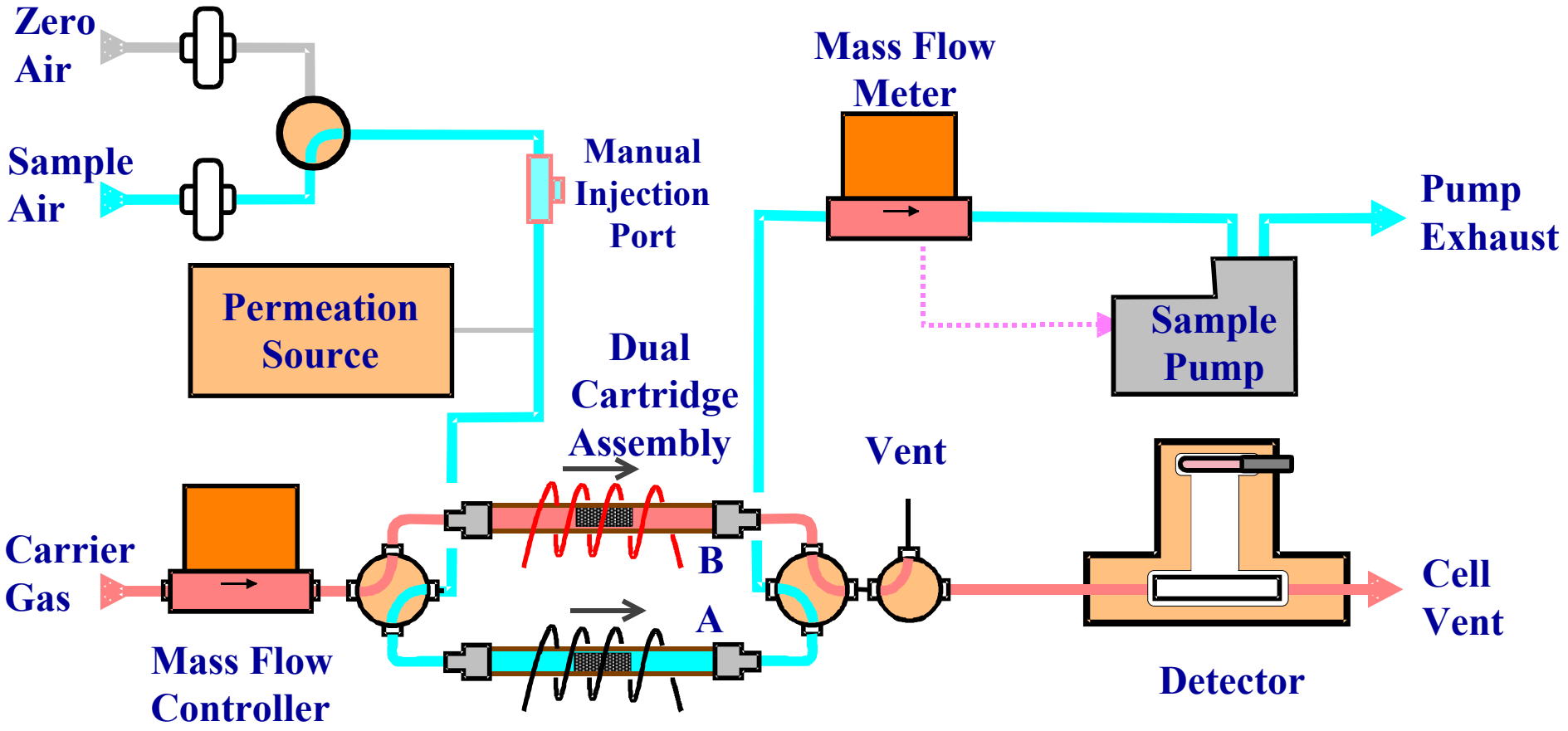
Sampling Box Heaters

Impactors

Analysis of Manual Denuder



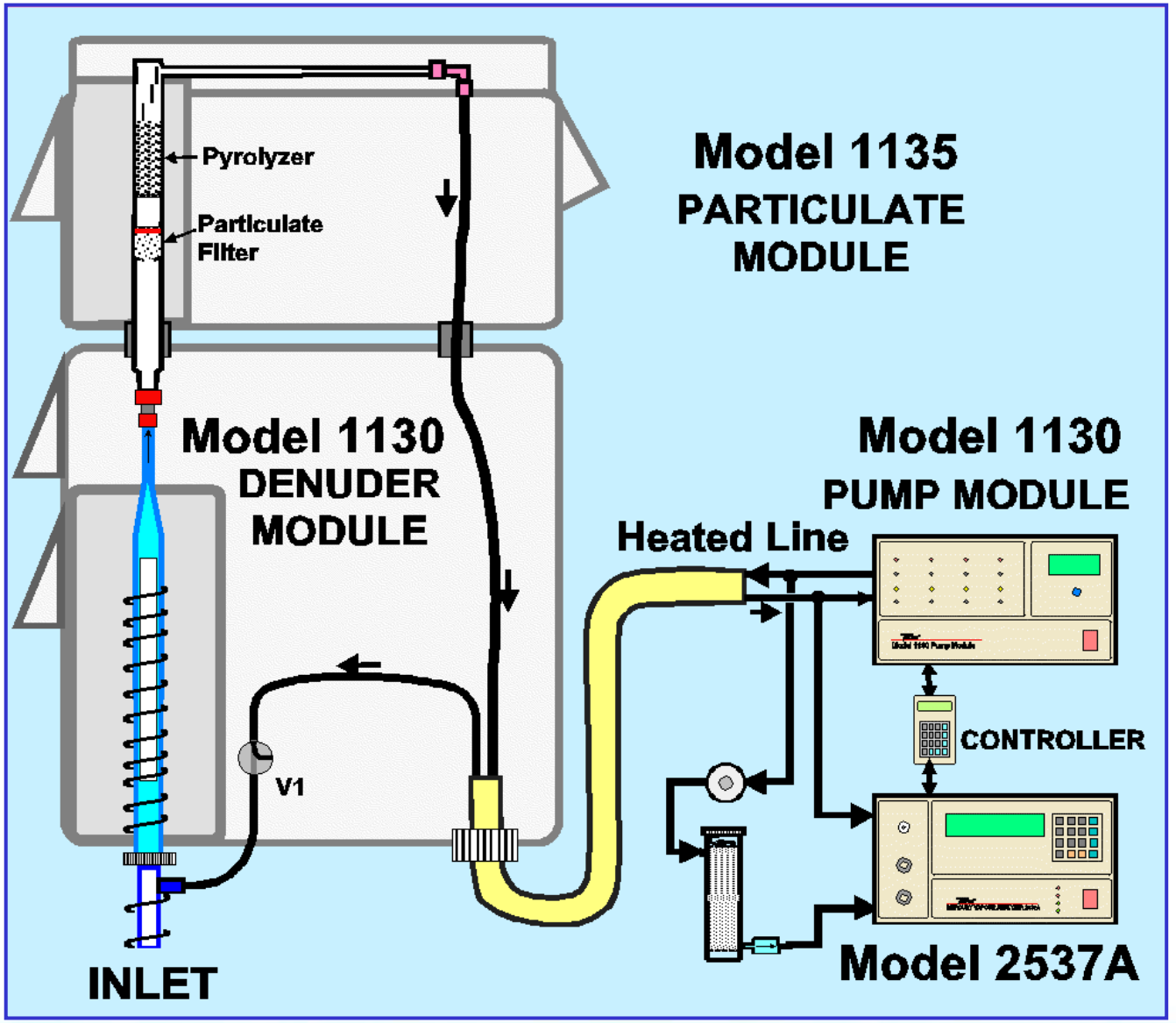
Flow Diagram of Tekran 2537A Mercury Analyzer



Tekran System Description

- **Model 2537A Vapor Phase Mercury Analyzer**
  - Semi-continuous Hg^0 Measurements
  - Gold Traps for Hg^0 Pre-concentration
  - Cold Vapor Atomic Fluorescence Spectrometer
- **Model 1130 Speciation Unit**
  - KCl Thermal Annular Denuder (Hg^{2+})
  - Zero Air Source & Pumping Module
- **Model 1135 Particulate Unit**
  - Thermal Quartz Filter & Pyrolyzer Column

Automated Speciation Instrumentation

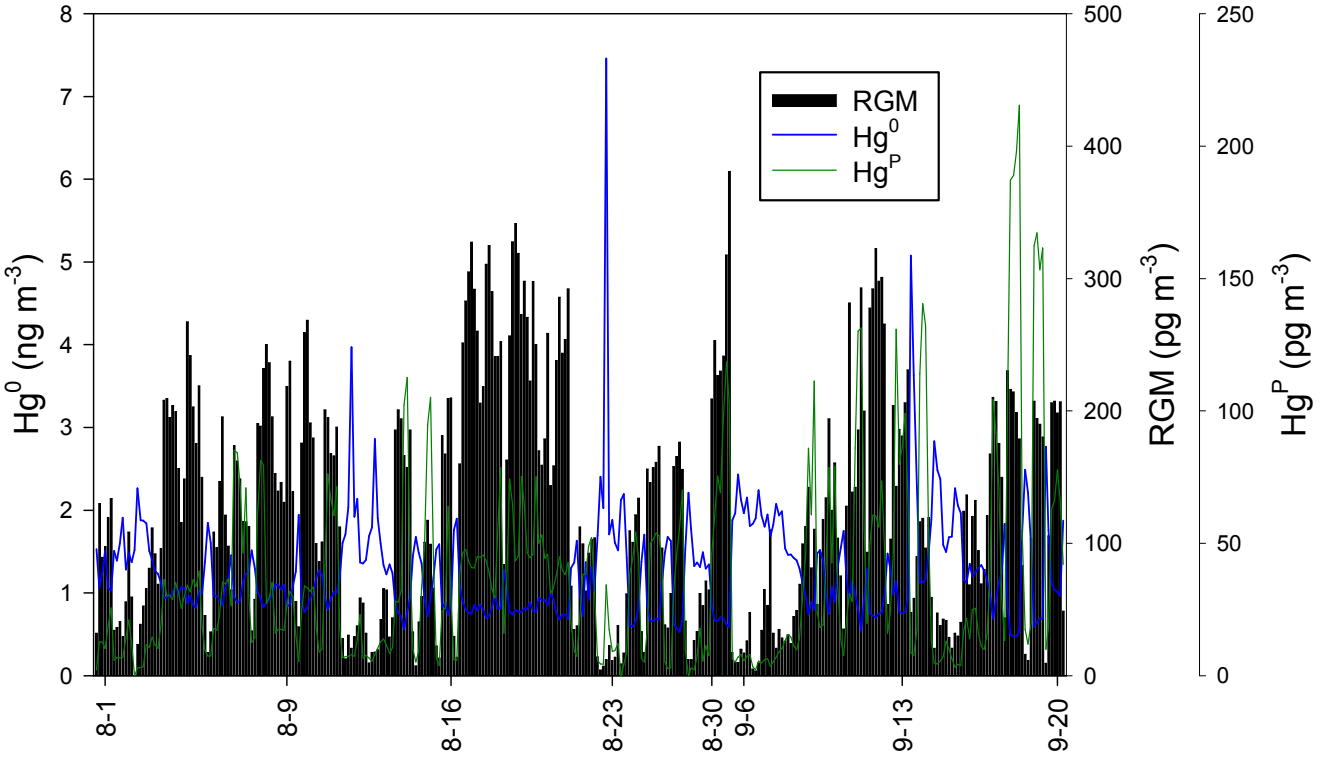


Typical External Installation

Typical Internal Installation

Mauna Loa Hg Time Series

7/31 – 9/20, 2001



Tekran System SOP

- Weekly
  - Replace: denuder, soda & lime trap, impactor frit, filters
  - Clean: inlet glassware, impactor, couplers
  - Check: trap performance, flows, heaters
  - Conduct perm tube calibration
- Monthly
  - Manual injections (2537A, 1130 inlet)
- Bi-monthly
  - Replace RPF, zero air filters
- Six Months
  - Calibrate 2537A permeation tube
- Annual
  - Replace: 1130 Carbon traps, pump brushes, 2537A lamp
  - Calibrate 2505 syringe, flow controllers

QA/QC Inlet Injection

Speciation Methods Summary

- KCl-Coated annular denuders quantity RGM without known interference problems when following SOP
- RGM is thermally (~500°C) converted to Hg^0
- Hg(p) is thermally (~800°C) converted to Hg^0
- Low denuder MDL's allow high-resolution sampling
- Manual method is inexpensive, simple, and mobile
- Tekran provides automated high-resolution data


Questions ???